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Synthesis and characterisation of four- and eight-membered ring auralactam complexes

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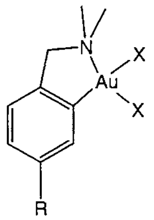
Abstract

The reactions of the cyclo-aurated gold(III) dihalide complex [$\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}AuCl_2$] with *N*-cyanoacetylurethane [$NCCH_2C(O)NHCO_2Et$], 2-benzoylacetanilide [$PhC(O)CH_2C(O)NHPh$] and acetoacetanilide [$MeC(O)CH_2C(O)NHPh$], and [$\{C_6H_4(CH_2NMe_2)\text{-}2\}AuCl_2$] with acetoacetanilide in dichloromethane with excess silver(I) oxide gives the first examples of auralactam complexes, containing $\overline{\text{Au–NR–C(O)–CHR}'}$ four-membered rings. A single-crystal X-ray diffraction study on the complex [$\{C_6H_4(CH_2NMe_2)\text{-}2\}\overline{Au\{NPhC(O)C}H(COMe)\}$] reveals similar structural features to related metallalactam complexes of platinum(II) and palladium(II). When a $CDCl_3$ solution of the complex [$\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}\overline{Au\{N(CO_2Et)C(O)C}HCN\}$] is allowed to stand for 18 h, a novel dimerisation reaction occurs, giving the insoluble product [$\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Au\{N(CO_2Et)C(O)CHCN\}]_2\cdot 2CDCl_3$, characterised by an X-ray structure determination. The dimer contains an eight-membered $\overline{\text{Au–N–C(O)–C–Au–N–C(O)–C}}$ ring. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gold; Metallacycle; Lactam; Dimerisation reaction; Crystal structures

1. Introduction

Small-ring metallacycles have attracted interest over a considerable period of time, for their basic structures and chemistry, and because metallacycles are involved in many metal-catalysed reactions of small molecules [1]. There is a very extensive metallacyclic chemistry of platinum(II) [2], but in marked contrast the chemistry of related metallacycles of isoelectronic gold(III) is scarcely developed. However, in recent years there has been much interest in the synthesis of gold(III) complexes, containing two cis halide ligands, together with an ancillary cyclometallated ligand which provides stability to the gold(III) centre, moderating its oxidising tendencies [3]. Such complexes, e.g. **1a** [4] and **1b** [5] are ideal precursors for the study of auracyclic chemistry, and recently we and others have described the syntheses of a range of four-membered ring complexes, including the first examples of auracyclobutane **2** [6], aurau-reylene **3** [7], and auracyclobutan-3-one **4** [8] ring systems, as well as other related metallacyclic complexes [8,9]. Complexes **1** generally appear to mimic the chemistry of related platinum(II) complexes with *cis*-halide ligands, such as *cis*-[$PtCl_2(PPh_3)_2$], but the reactivity towards thioureas in the presence of Ag_2O base has been found to be very different. With platinum(II), four-membered metallacycles, e.g. **5** are formed [10], but with the gold(III) complexes **1a** and **1b** desulfurisation of the (1,3-dimethyl)thiourea occurs, giving complex gold–silver–sulfide–halide aggregate cations [11]. This suggests that while there may be many similarities between metallacycles of platinum(II) and gold(III), differences are also to be expected.



1a, R = H, X = Cl
1b, R = OMe, X = Cl
1c, R = H, X = OAc

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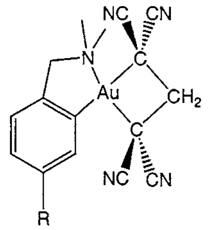

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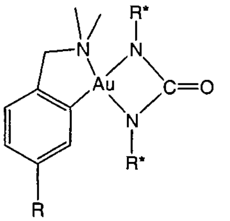

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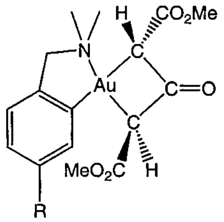
R = H, OMe
R* = Ph, C(O)CH$_3$



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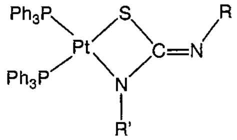

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Previously we have synthesised metallalactam complexes of platinum(II) and palladium(II) by reaction of metal dihalide complexes with *N*-cyanoacetylurethane [12,13], 2-benzoylacetanilide [14], acetoacetanilide [15], or cyanoacetylurea [16] in the presence of silver(I) oxide base. In this paper we report the synthesis of the first examples of auralactam complexes using the same methodology. Surprisingly, few gold(III) complexes containing amide (amidate) ligands appear to have been reported [17], though such species may be important in the metabolism of gold(I) drugs [18].

2. Results and discussion

2.1. Synthesis and characterisation of four-membered ring auralactam complexes

The reactions of the gold(III) dichloride complex **1b** with *N*-cyanoacetylurethane, 2-benzoylacetanilide or acetacetanilide, and **1a** with acetoacetanilide in refluxing dichloromethane in the presence of excess silver(I) oxide gave good yields of the auralactam complexes **6a**–**6d**. The complexes are all soluble in polar organic

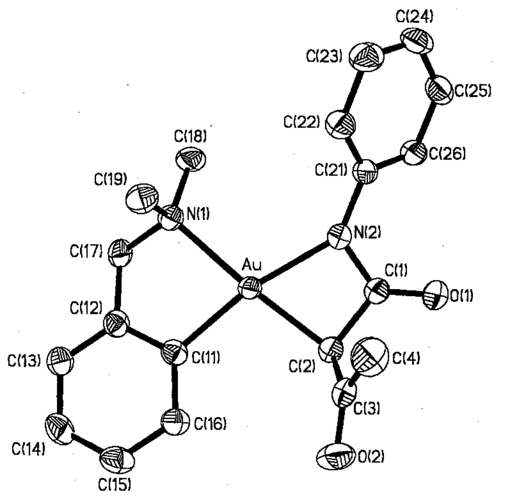
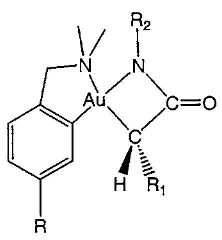


Fig. 1. Molecular structure and atom labelling scheme of [{C$_6$H$_4$(CH$_2$NMe$_2$)-2}Au{NPhC(O)CH(COMe)}] (**6d**). Thermal ellipsoids are at the 50% probability level, and hydrogen atoms are not shown.

Table 1
Selected bond lengths (Å) and angles (°) for [{C$_6$H$_4$(CH$_2$NMe$_2$)-2}Au{NPhC(O)CH(COMe)}] (**6d**)

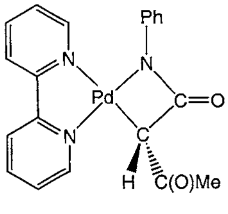
Au–C(11)	2.027(3)	Au–C(2)	2.076(3)
Au–N(2)	2.097(3)	Au–N(1)	2.157(3)
Au···C(1)	2.616(3)	O(1)–C(1)	1.226(4)
N(2)–C(1)	1.356(4)	N(2)–C(21)	1.425(4)
C(1)–C(2)	1.536(5)	C(2)–C(3)	1.495(5)
O(2)–C(3)	1.220(5)	C(3)–C(4)	1.504(6)
C(11)–Au–C(2)	102.06(13)	C(11)–Au–N(2)	168.64(12)
C(2)–Au–N(2)	66.65(12)	C(11)–Au–N(1)	81.74(12)
C(2)–Au–N(1)	174.54(12)	N(2)–Au–N(1)	109.42(11)
C(1)–N(2)–C(21)	123.4(3)	C(1)–N(2)–Au	96.1(2)
C(21)–N(2)–Au	140.5(2)	O(1)–C(1)–N(2)	130.3(3)
O(1)–C(1)–C(2)	124.9(3)	N(2)–C(1)–C(2)	104.7(3)
O(1)–C(1)···Au	174.9(3)	C(3)–C(2)–C(1)	113.7(3)
C(2)–C(3)–C(4)	118.5(3)	C(1)–C(2)–Au	91.5(2)
C(3)–C(2)–Au	113.8(2)	O(2)–C(3)–C(4)	120.0(4)
O(2)–C(3)–C(2)	121.5(4)		



6a, R = OMe, R$_1$ = CN, R$_2$ = CO$_2$Et
6b, R = OMe, R$_1$ = COPh, R$_2$ = Ph
6c, R = OMe, R$_1$ = COMe, R$_2$ = Ph
6d, R = H, R$_1$ = COMe, R$_2$ = Ph

solvents such as dichloromethane, and are relatively stable, but turn purple on prolonged storage in air at room temperature, especially when exposed to sunlight. When complex **6a** is allowed to stand overnight in $CDCl_3$, it dimerises to form an insoluble product, which is discussed in Section 2.2.

A single-crystal X-ray diffraction study has been carried out on complex **6d**; the molecular structure is shown in Fig. 1, while Table 1 gives selected bond lengths and angles. The structure shows a distorted square-planar gold(III) centre, which is part of the four-membered lactam ring. The largest deviation from the Au, N(1), N(2), C(2), C(11) least-squares plane is 0.041(1) Å for Au. The bond angles about the gold centre deviate considerably from an idealised square-planar geometry, the largest distortion being the constricted N(2)–Au–C(2) 'bite' angle of 66.65(12)°. Similar acute angles around 67° have been observed for platina- and palladalactam complexes [12,14,15]. The gold–carbon bond lengths reflect the different hybridisation of the carbon atoms, with the gold–sp^2 carbon bond Au–C(11) being shorter [2.027(3) Å] than the gold–sp^3 carbon [Au–C(2) 2.076(3) Å]. The gold–nitrogen bonds also differ, with the Au–N(1) dative bond being longer [2.157(3) Å] than the Au–N(2) covalent bond [2.097(3) Å]. The Au–N(2) bond is longer than the Pd–N(lactam) bond in the analogous palladium complex **7** [2.033(9) Å] [15], partly due to the high *trans*-influence of the aryl carbon compared to bipyridyl, since the radius of Au(III) is normally only about 0.02 Å greater than that of Pd(II) (e.g. the Au–Cl bonds in Ph_3PAuCl_3 [19] are 0.02 Å on average longer than the Pd–Cl bonds in $[Ph_3PPdCl_3]^-$ [20]).



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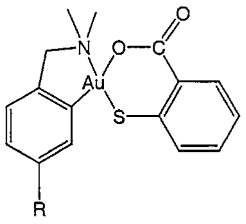
The auralactam ring is slightly puckered, with an angle of 10.5(4)° between the Au, N(2), C(2) and N(2), C(1), C(2) planes; the fold angle is similar to those of related platina- and palladalactam complexes. The complex is the expected isomer with the two low *trans*-influence N atoms mutually *cis*, due to antisymbiosis [21]. This is also found for other gold(III) complexes, including thiosalicylate complexes **8**, where the low *trans*-influence O and N atoms are mutually *cis* [22]. The Cl atom trans to the high *trans*-influence aryl carbon of **1** would be expected to be the most labile, and substituted first. The nitrogen of the organic reagent is expected to bond to the gold centre initially via nitrogen, giving an intermediate complex such as **9**, since in the reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with *N*-cyanoacetylurethane, the nitrogen-bonded intermediate **10** was able to be isolated [23]. Cyclisation of **9** would then occur, giving the observed isomer of complexes **6**.



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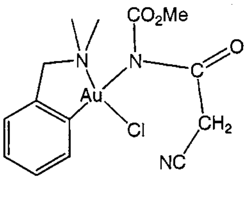
R = H, OMe



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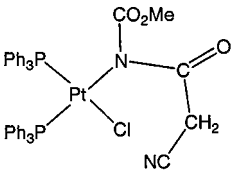

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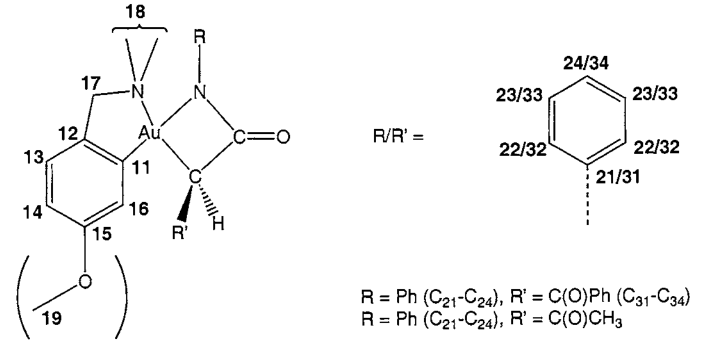
The geometry of the cyclo-aurated *N*,*N*-dimethylbenzylamine ligand is similar to those of previously reported complexes. The ligand bite angle N(1)–Au–C(11) [81.74(12)°] approaches the ideal 90°. Compensating for the two acute bond angles of the ring systems, the N(1)–Au–N(2) and C(11)–Au–C(2) bond angles are more obtuse [109.42(11) and 102.06(13)°, respectively]. The five-membered ring formed by Au–C(11)–C(12)–C(17)–N(1) has a significant fold angle [34.9(2)°] between the planes defined by Au–C(11)–C(12)–N(1) and N(1)–C(12)–C(17)–C(11).

The NMR spectra of complexes **6** show the expected features. Due to the presence of two different groups on the gold-bonded quaternary carbon, the benzylic CH_2 protons are non-equivalent and give an AB spin system of two doublets. The same inequivalency is also expected for the NMe_2 groups; for complexes **6b**, **6c** and **6d** the two signals were resolved in their ^1H-NMR spectra, but in complex **6a** they were not resolved, and appeared as a broadened singlet. Separate NMe resonances were also observed in the ^{13}C-NMR spectra of **6a**–**6d**, typically separated by 0.1–0.2 ppm. Similar effects were observed previously for the *cyclo*-octadiene CH groups of platinalactam complexes [12]. In com-

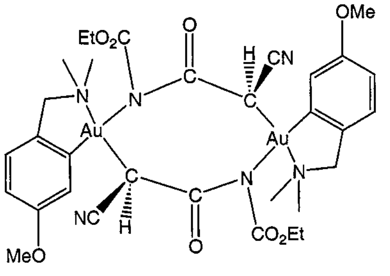


Scheme 1.

plexes **6a**, **6b** and **6c**, two of the three aromatic proton signals (H_{14} and H_{16}, Scheme 1) show long range ^4J(HH) ('W') coupling, of 2–3 Hz.

2.2. Formation and characterisation of the dimeric complex *11*

On standing a $CDCl_3$ solution of the auralactam complex **6a** overnight, colourless crystals were deposited, which were insoluble in all common solvents tested, e.g. chloroform and methanol. Due to this insolubility, it was not possible to obtain NMR or electrospray mass spectra. In order to characterise the product, a single-crystal X-ray diffraction study was carried out. The molecular structure of **11** and atom numbering scheme (Fig. 2) show that the product is a dimer, containing an eight-membered ring system and two gold atoms. The molecule crystallises about the crystallographic inversion centre, with a molecule of $CDCl_3$ per asymmetric unit. Table 2 gives selected bond lengths and angles for **11**.



11

The coordination sphere around the gold(III) centre is a slightly distorted square plane with no atom displaced more than 0.071(1) Å (Au) from the plane. The gold–nitrogen bonds are slightly longer [Au–N(3) 2.116(3), Au–N(1) 2.137(3) Å] than the gold–carbon bonds [Au–C(11) 2.031(3), Au–C(2′) 2.098(3) Å]. As with the four-membered ring auralactam **6d**, the longer Au–N bond occurs for the NMe_2 group. The less-constrained geometry in the eight-membered ring is reflected in the bond angles around the gold atom compared to the four-membered auralactam **6d**. The most acute angle is 81.78(11)° for C(11)–Au–N(1), which is part of the five-membered ring formed by the cyclometallated benzylamine ligand. As with **6d**, this five-membered ring shows puckering, with a fold angle of 39.1(2)° through the Au, N(1), C(11), C(12) and the C(12), C(17), N(1) planes.

The plane of the bridging cyanoacetylurethane group lies almost perpendicular [83.82(5)°] to the gold coordination plane. In **11**, the atoms of the cyanoacetylurethane ligand are twisted about the plane of the ligand, which may be to accommodate the eight-membered metallacycle. Thus, the atoms N(3), O(2), O(4), C(3), C(4), C(5) and C(6) are effectively coplanar, with a maximum deviation of 0.094(3) Å [for C(4)], while the cyanide group is skewed from the plane of the ligand. Atom N(2) lies 0.232(10) Å out of this plane. The urethane carbonyl oxygen O(3) is twisted with respect to the plane, and lies 0.234(7) Å outside the mean plane.

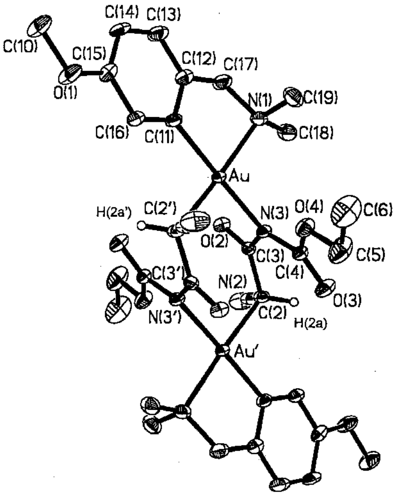


Fig. 2. Molecular structure of $[\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Au\{N(CO_2Et)C(O)CHCN\}]_2 \cdot 2CDCl_3$ (**11**), with atom numbering scheme. Thermal ellipsoids are displayed at the 50% probability level, and hydrogen atoms [except H(2a) and H(2a)′] and $CDCl_3$ molecules of crystallisation are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for $[\{C_6H_3(CH_2NMe_2)$-2-(OMe)-5$\}Au\{N(CO_2Et)C(O)CH(CN)\}]_2\cdot 2CDCl_3$ (**11**)

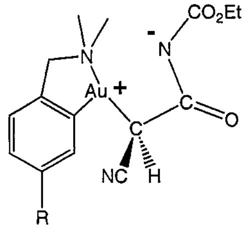
Au–C(11)	2.031(3)	Au–C(2′)	2.098(3)
Au–N(3)	2.116(3)	Au–N(1)	2.137(3)
C(2)–Au′	2.098(3)	N(3)–C(4)	1.384(4)
N(2)–C(1)	1.152(5)	O(3)–C(4)	1.211(4)
N(3)–C(3)	1.374(4)	O(4)–C(5)	1.450(4)
O(2)–C(3)	1.237(4)	C(2)–C(3)	1.523(4)
O(4)–C(4)	1.353(4)	C(5)–C(6)	1.499(5)
C(1)–C(2)	1.464(4)		
C(11)–Au–C(2′)	92.89(12)	C(11)–Au–N(3)	175.52(10)
C(2′)–Au–N(3)	90.53(10)	C(11)–Au–N(1)	81.78(11)
C(2′)–Au–N(1)	173.03(10)	N(3)–Au–N(1)	95.04(9)
C(3)–N(3)–C(4)	124.3(2)	C(3)–N(3)–Au	114.3(2)
C(4)–N(3)–Au	119.8(2)	N(2)–C(1)–C(2)	178.7(3)
C(4)–O(4)–C(5)	115.7(2)	C(1)–C(2)–Au′	106.2(2)
C(1)–C(2)–C(3)	108.9(2)	O(2)–C(3)–N(3)	118.7(3)
C(3)–C(2)–Au′	111.0(2)	N(3)–C(3)–C(2)	121.6(3)
O(2)–C(3)–C(2)	119.6(3)	O(3)–C(4)–N(3)	128.5(3)
O(3)–C(4)–O(4)	123.6(3)	O(4)–C(5)–C(6)	107.1(3)
O(4)–C(4)–N(3)	107.8(2)		

The chloroform of crystallization in the lattice forms a weak bond to O(2), with C–H 0.99 Å, O···H 2.30 Å and the C–H···O angle 152.6°.

2.3. Discussion

It is possible to speculate on the mechanism and driving force for the dimerisation reaction. The gold–N(CO_2Et) bond of **6a** is *trans* to the very high *trans*-influence aurated phenyl ring, and so the Au–N bond may break, giving a zwitterionic intermediate **12**. The gold(III) centre is more labile than platinum(II); rates of cyanide exchange indicate that the lability of gold(III) is about two orders of magnitude greater than that of platinum(II) [24]. Additionally, Parish and coworkers have found that in the complex **1c** one of the acetate ligands (*trans* to the aryl group) undergoes exchange more rapidly than the acetate group *trans* to the NMe_2 group [25]. The relief of some ring strain in the four-membered ring will assist the ring opening; recall that the N–Au–C bond angle in the four-membered ring of **6d** is 66.65(12)°, but in the dimer **11** it is 90.53(10)°. In **12**, the negative charge on N can be resonance stabilised by the two adjacent carbonyl groups, and in this regard it is noteworthy that a dimeric species was only observed from complex **6a**, and not **6b**–**6d**, where less electron-withdrawing phenyl groups are bonded to the lactam nitrogen. Head-to-tail dimerisation of two intermediates **12** could then give the observed dimer **11**, promoted by its insolubility.

In conclusion, we have synthesised the first examples of auralactam complexes; the structure of one of these shows it to be similar to other platina– and pallada–lactam complexes. The formation of a novel dimeric complex has also been observed, indicating that the chemistry of gold(III) shows more variation than that of the isoelectronic platinum(II), and suggests that the metallacyclic chemistry of gold(III) is worthy of detailed investigations.



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3. Experimental

3.1. Materials and instrumentation

The complexes $[\{C_6H_4(CH_2NMe_2)$-2$\}AuCl_2]$ (**1a**) [4] and $[\{C_6H_3(CH_2NMe_2)$-2-(OMe)-5$\}AuCl_2]$ (**1b**) [5] were prepared by literature methods. *N*-Cyanoacetylurethane, 2-benzoylacetanilide and acetoacetanilide were used as supplied by Aldrich. Dichloromethane and light petroleum (b.p. 40–60°C) were distilled from CaH_2 prior to use, and Et_2O was distilled from sodium benzophenone ketyl. All reactions were carried out under a nitrogen atmosphere, and were shielded from light.

^1H-NMR spectra were recorded at 300.133 MHz on a Bruker AC300P instrument, or at 400.131 MHz on a Bruker DRX instrument. ^{13}C-NMR spectra were obtained at either 75.47 or 100.61 MHz on the same instruments. A combination of DEPT-135, $^{13}C-^1H$ correlation, heteronuclear multiple quantum correlation (HMQC), and heteronuclear multiple bond correlation (HMBC) techniques were used to assign individual resonances. The ROESY technique was used to assign the aromatic resonances of complex **6b**. The atom numbering used is given in Scheme 1. Electrospray mass spectra were recorded on a VG Platform II instrument in positive-ion mode, in 1:1 MeCN–H_2O. Infrared spectra were recorded as KBr disks on a Bio-Rad FTS40 spectrometer. Melting points were determined on a Reichert–Jung hotstage apparatus and are uncorrected.

3.2. Synthesis of $[\{C_6H_3(CH_2NMe_2)$-2-(OMe)-5$\}Au\{N(CO_2Et)C(O)CHCN\}]$ (*6a*)

A mixture of $[\{C_6H_3(CH_2NMe_2)$-2-(OMe)-5$\}AuCl_2]$ (46 mg, 0.11 mmol), *N*-cyanoacetylurethane (17 mg, 0.11 mmol) and silver(I) oxide (45 mg, excess) in deoxygenated CH_2Cl_2 (20 ml) was refluxed for 3 h. The silver salts were removed by filtration with no precautions to exclude air, and the solvent removed from the filtrate to give a pale tan solid. The product was recrystallised from CH_2Cl_2–light petroleum to give 46 mg (83%) of **6a**. Found: C, 36.5; H, 3.8; N, 8.0; $C_{16}H_{20}N_3AuO_4$ requires C, 37.3; H, 3.9; N, 8.2%. IR: ν(CN) 2224(s); ν(CO) 1746(s), 1700(s) cm^{-1}. M.p. (dec.) 210–213°C. ES-MS (cone voltage 20 V): m/z 516 $[M+H]^+$ (100%), 533 $[M+NH_4]^+$ (30%), 1048 $[2M+NH_4]^+$ (90%). ^1H-NMR, δ 7.10 [d, 1H, H_{13}, $^3J(H_{13}, H_{14})$ 8], 7.05 [d 1H, H_{16}, $^4J(H_{16}, H_{14})$ 2], 6.81 [dd, 1H, H_{14}, $^3J(H_{14}, H_{13})$ 8, $^4J(H_{14}, H_{16})$ 2], 4.26 [q, 2H, ethyl CH_2, $^3J(H, H)$ 7], 4.16 [d, 2H, $H_{17a,b}$, $^2J(H_a, H_b)$ 2], 3.81 (s, 3H, H_{19}), 3.26 (s, 6H, H_{18}), 1.67 (s, 1H, Au–C*H*), 1.35 [t, 3H, ethyl C*H*$_3$, $^3J(H, H)$ 7]. ^{13}C-{^1H}-NMR, δ 166.0 [s, ring C(O)], 158.6 (s, C_{12}), 139.5 [s, ester *C*(O)], 138.2 (s, C_{11}), 124.1 (s, C_{15}), 117.4 (s, C_{13}), 117.2 (s, C_{16}), 116.1 (s, CN), 114.5 (s, C_{14}), 72.4 (s, C_{17}), 62.5 (s, ethyl *C*H_2), 55.6 (s, C_{19}), 51.8 (s, C_{18a}), 51.7 (s, C_{18b}), 18.4 (s, Au–CH), 14.5 (s, ethyl *C*H_3).

3.3. Preparation of [{$C_6H_3(CH_2NMe_2)$-2-(OMe)-5}-Au{NPhC(O)CHC(O)Ph}] (**6b**)

[{$C_6H_3(CH_2NMe_2)$-2-(OMe)-5}$AuCl_2$] (52 mg, 0.120 mmol), 2-benzoylacetanilide (29 mg, 0.122 mmol) and silver(I) oxide (62 mg, excess) were refluxed in degassed CH_2Cl_2 (20 ml) for 2.5 h. Removal of the silver salts by filtration gave a deep yellow solution. Removal of the solvent resulted in a dark tan solid, which was recrystallised by addition of light petroleum (30 ml) to a CH_2Cl_2 (2 ml) solution. This product was filtered and dried in vacuo to give **6b** (48 mg, 66%). Found: C, 50.4; H, 4.2; N, 4.8; $C_{25}H_{25}N_2AuO_3$ requires: C, 50.2; H, 4.2; N, 4.7%. IR: ν(CO) 1643(vs) cm^{-1}. M.p. (dec.) 197–201°C. ^1H-NMR, δ 8.17 [dd, 2H, H_{32}, $^3J(H_{32}, H_{33})$ 8, $^4J(H_{33}, H_{34})$ 2], 7.50 [t, 1H, H_{34}, $^3J(H_{34}, H_{33})$ 7, $^4J(H_{34}, H_{32})$ 2], 7.43 [dist. t, 2H, H_{23}, $^3J(H_{23}, H_{22/24})$ 8], 7.35 [dist. t, 2H, H_{33}, $^3J(H_{33}, H_{32/34})$ 8], 7.24 [d, 2H, H_{22}, $^3J(H_{22}, H_{23})$ 8, $^4J(H_{22}, H_{24})$ 1], 7.11 [t, 1H, H_{24}, $^3J(H_{24}, H_{23})$ 8), $^4J(H_{24}, H_{22})$ 1], 6.98 [d, 1H, H_{13}, $^3J(H_{13}, H_{14})$ 8], 6.72 [d, 1H, H_{16}, $^4J(H_{16}, H_{14})$ 3], 6.64 [dd, 1H, H_{14}, $^3J(H_{14}, H_{13})$ 8, $^4J(H_{14}, H_{16})$ 3], 4.19 (s, Au-C*H*), 3.93 [AB spin system, 2H, $H_{17a,b}$, $^2J(H_a, H_b)$ 37], 3.51 (s, 3H, H_{19}), 2.75 (s, 3H, H_{18}), 2.74 (s, 3H, H_{18}). ^{13}C-{^1H}-NMR, δ 196.9 [s, *C*(O)Ph], 170.3 [s, ring *C*(O)], 158.2 (s, C_{12}), 141.9 (s, C_{11}), 141.5 (s, C_{21}), 138.8 (s, C_{31}), 137.6 (s, C_{15}), 132.6 (s, C_{34}), 129.2 (s, C_{33}), 129.0 (s, C_{32}), 128.5 (s, C_{23}), 126.4 (s, C_{22}), 125.1 (s, C_{24}), 124.1 (s, C_{13}), 117.6 (s, C_{16}), 114.1 (s, C_{14}), 71.5 (s, C_{17}), 55.2 (s, C_{19}), 50.8 (s, C_{18a}), 50.7 (s, C_{18b}), 44.4 (s, Au–*C*H).

3.4. Preparation of [{$C_6H_3(CH_2NMe_2)$-2-(OMe)-5}Au{NPhC(O)CHC(O)CH_3}] (**6c**)

A mixture of [{$C_6H_3(CH_2NMe_2)$-2-(OMe)-5}$AuCl_2$] (52 mg, 0.120 mmol), acetoacetanilide (23 mg, 0.130 mmol) and silver(I) oxide (23 mg, excess) in deoxygenated CH_2Cl_2 (20 ml) was refluxed for 4 h. The silver salts were removed by filtration in air affording a light brown solution. The solvent was removed giving the crude product, which was redissolved in CH_2Cl_2 (ca. 3 ml) and precipitated by the addition of Et_2O (ca. 50 ml). The tan precipitate of **6c** was filtered and dried (40 mg, 63%). Found: C, 44.9; H, 4.1; N, 5.6; $C_{20}H_{23}N_2AuO_3$ requires: C, 44.8; H, 4.3; N, 5.2%. IR: ν(CO) 1641(s) cm^{-1}. M.p. (dec.) 186–191°C. ^1H-NMR, δ 7.38 [t, 2H, H_{23}, $^3J(H_{23}, H_{22/24})$ 8], 7.22 [dd, 2H, H_{22}, $^3J(H_{22}, H_{23})$ 8, $^4J(H_{22}, H_{24})$ 1], 7.14 [t, 1H. H_{24}, $^3J(H_{24}, H_{23})$ 8, 7.09 [d, 1H, H_{16}, $^4J(H_{16}, H_{14})$ 2], 7.06 [d, 1H, H_{13}, $^3J(H_{13}, H_{14})$ 8], 6.74 [dd, 1H, H_{14}, $^3J(H_{14}, H_{13})$ 8, $^4J(H_{14}, H_{16})$ 2], 4.00 [d, AB spin system, 2H, $H_{17a,b}$, $^2J(H_a, H_b)$ 14], 3.86 (s, 3H, H_{19}), 3.41 (s, 1H, Au-C*H*), 2.82 (s, 3H, H_{18}), 2.79 (s, 3H, H_{18}), 2.41 [s, 3H, C(O)C*H*$_3$]. ^{13}C-{^1H}-NMR, δ 203.1 [s, *C*(O)CH_3], 170.4 [s, ring *C*(O)], 158.5 (s, C_{12}), 141.7 (s, C_{11}), 141.3 (s, C_{21}), 137.4 (s, C_{15}), 129.2 (s, C_{23}), 126.4 (s, C_{22}), 125.2 (s, C_{24}), 123.9 (s, C_{13}), 116.9 (s, C_{16}), 114.3 (s, C_{14}), 71.5 (s, C_{17}), 55.6 (s, O*C*H_3), 50.9 (s, C_{18a}), 50.8 (s, C_{18b}), 48.2 (s, Au–*C*H), 27.7 [s, C(O)CH_3].

3.5. Preparation of [{$C_6H_4(CH_2NMe_2)$-2}Au{NPhC(O)CH(COMe)}] (**6d**)

A deoxygenated mixture of [{$C_6H_4(CH_2NMe_2)$-2}$AuCl_2$] (34 mg, 0.084 mmol), acetoacetanilide (16 mg, 0.089 mmol) and silver(I) oxide (ca. 100 mg, excess) in CH_2Cl_2 (20 ml) was refluxed for 2.5 h. Silver salts were removed by filtration affording a pale yellow solution. The solvent was removed and the tan product recrystallised by addition of Et_2O (ca. 40 ml) to a CH_2Cl_2 (3 ml) solution, to give **6d** (60 mg, 36%). Crystals of single crystal X-ray diffraction quality were grown by vapour diffusion of Et_2O into a CH_2Cl_2 solution. Found: C, 45.0; H, 4.1; N, 5.7; $C_{19}H_{21}AuN_2O_2$ requires: C, 45.1; H, 4.2; N, 5.5%. IR: ν(CO) 1641(s) cm^{-1}. ESMS (cone voltage 20 V): m/z 507 $[M+H]^+$ (100%), 1013 $[2M+H]^+$ (40%). M.p. (dec.) 184–187°C. ^1H-NMR, δ 7.45 [d, H_{15}, $^3J(H, H)$ 7], 7.37 [dist. t, H_{23}, $^3J(H, H)$ 7], 7.21 [dd, H_{22}, $^3J(H, H)$ 7], 7.20 [dist t, H_{24}, $^3J(H, H)$ 8], 7.15 [t, H_{16}, $^3J(H, H)$ 7], 7.15 [t, H_{13}, $^3J(H, H)$ 8], 7.13 [t, H_{14}, $^3J(H, H)$ 8], 4.04 [AB spin system, 2H, $H_{17a,b}$, $^2J(H_a, H_b)$ 33], 3.40 (s, 1H, Au-C*H*), 2.83 (s, 3H, H_{18}), 2.79 (s, 3H, H_{18}), 2.40 [s, 3H, C(O)C*H*$_3$]. ^{13}C-{^1H}-NMR, δ 201.3 [s, *C*(O)CH_3], 169.5 [s, ring *C*(O)], 146.4 (s, C_{12}), 145.4 (s, C_{21}), 133.2 (s, C_{11}), 132.6 (s, C_{15}), 128.5 (s, C_{23}), 128.1 (s, C_{13}), 127.4 (s, C_{24}), 123.9 (s, C_{22}), 123.5 (s, C_{14}), 122.6 (s, C_{16}), 72.8 (s, C_{17}), 52.0 (s, C_{18a}), 51.8 (s, C_{18b}), 48.4 (s, Au–*C*H), 14.5 [s, C(O)*C*H_3].

Table 3
Crystal, collection and refinement data for [{$C_6H_4(CH_2NMe_2)$-2}Au{NPhC(O)CH(COMe)}] (**6d**) and [{$C_6H_4(CH_2NMe_2)$-2-(OMe)-5} Au {N(CO_2Et)C(O)CH(CN)}]$_2$·2$CDCl_3$ (**11**)

	6d	**11**
Crystal data		
Empirical formula	$C_{19}H_{21}AuN_2O_2$	$C_{16}H_{20}AuN_3O_4 \cdot CDCl_3$
Formula weight	506.34	636.70
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	8.721(1)	12.359(1)
b (Å)	10.7841(1)	15.1831(1)
c (Å)	11.0297(1)	12.5665(1)
α (°)	61.6520(1)	90
β (°)	84.37(1)	113.740(1)
γ (°)	79.537(1)	90
V (Å^3)	897.662(12)	2158.52(2)
Z	2	4
D_{calc} (g cm^{-3})	1.873	1.959
Data collection		
Crystal size (mm)	$0.40 \times 0.30 \times 0.22$	$0.34 \times 0.30 \times 0.22$
Theta range for data collection (°)	2.10–28.13	1.80–28.17
Reflections collected	8901	5196
Independent reflections	3935 [$R_{int} = 0.0193$]	4955 [$R_{int} = 0.0193$]
Absorption coefficient (mm^{-1})	8.207	7.211
Max/min transmission	0.2654, 0.1378	0.2998, 0.1929
F(000)	488	1228
Structure analysis and refinement		
Solution by	Patterson methods	Direct methods
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3935/0/220	4955/0/251
Goodness-of-fit on F^2	1.104	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0188$, $wR_2 = 0.0475$	$R_1 = 0.0213$, $wR_2 = 0.0524$
R indices (all data)	$R_1 = 0.0197$, $wR_2 = 0.0480$	$R_1 = 0.0236$, $wR_2 = 0.0536$
Weighting scheme [a]	$w = 1/[\sigma^2(F_o^2) + (0.0135P)^2 + 1.1058P]$	$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 3.6911P]$
Largest difference peak (e Å^{-3})	1.845	1.257
Largest difference hole (e Å^{-3})	−1.087	−1.663
Solution by	SHELXS 97 [27]	SHELXS 96 [27]
Refinement by	SHELXL 97 [27]	SHELXL 97 [27]

[a] $P = (F_o^2 + 2F_c^2)/3$.

3.6. X-ray crystallography

Data were collected on a Siemens SMART CCD diffractometer for **6d** and on an Enraf–Nonius CAD4 diffractometer for **11** using Mo–K_α radiation ($\lambda = 0.71073$ Å) at 203(2) K, and were corrected for absorption using SADABS [26]. Cell and final refinement parameters for both structures are given in Table 3.

3.6.1. Complex **6d**

The location of the gold atom was determined by Patterson methods. Remaining atoms were located from residual electron-density maps, and refined routinely. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, with U_{iso} 1.5 times that of the atom to which they are bonded (for methyl hydrogens) and 1.2 times for all other hydrogen atoms.

3.6.2. Complex **11**

Colourless crystals of the dimer precipitated from an NMR solution of **6a** in $CDCl_3$ during an 18-h data collection. Colloidal gold and/or silver (from the Ag_2O reagent) was also observed, indicating some decomposition. Energy dispersive X-ray (EDAX) analysis of a crushed crystal of **11** on a scanning electron microscope indicated the presence of Au and Cl.

Atoms not located in the initial electron density map were located from subsequent electron density maps. All heavy atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with methyl hydrogens assigned thermal parameters 1.5 times the U_{iso} of the atom to which they are bonded, and all others with thermal parameters 20% greater than the U_{iso} of the atom to which they are bonded.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, no. 149443 for compound **6d**, and no. 149444 for compound **11**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) J. Cámpora, M. Paneque, M.L. Poveda, E. Carmona, Synlett (1994) 465. (b) M. Lautens, W. Klute, W. Tam, Chem. Rev. 96 (1996) 49. (c) M. Catellani, G.P. Chiusoli, M. Costa, J. Organomet. Chem. 500 (1995) 69. (d) N. Basickes, A. Sen, Polyhedron 14 (1995) 197. (e) G. Dyker, Chem. Ber./Recueil 130 (1997) 1567. (f) X. Yin, J.R. Moss, Coord. Chem. Rev. 181 (1999) 27. (g) J. Feldman, R.R. Schrock, Prog. Inorg. Chem. 39 (1991) 1. (h) G. Dyker, J. Körning, F. Nerenz, P. Siemsen, S. Sostmann, A. Wiegand, P.G. Jones, P. Bubenitschek, Pure Appl. Chem. 68 (1996) 323. (i) W. Leitner, Coord. Chem. Rev. 153 (1996) 257.

[2] (a) S.D. Chappell, D.J. Cole-Hamilton, Polyhedron 1 (1982) 739. (b) R.J. Puddephatt, Coord. Chem. Rev. 33 (1980) 149. (c) J. Cámpora, P. Palma, E. Carmona, Coord. Chem. Rev. 193–195 (1999) 207. (d) P.W. Jennings, L.L. Johnson, Chem. Rev. 94 (1994) 2241.

[3] (a) Y. Fuchita, H. Ieda, S. Wada, S. Kameda, M. Mikuriya, J. Chem. Soc. Dalton Trans. (1999) 4431. (b) Y. Fuchita, H. Ieda, A. Kayama, J. Kinoshita-Nagaoka, H. Kawano, S. Kameda, M. Mikuriya, J. Chem. Soc. Dalton Trans. (1998) 4095. (c) Y. Fuchita, H. Ieda, Y. Tsunemune, J. Kinoshita-Nagaoka, H. Kawano, J. Chem. Soc. Dalton Trans. (1998) 791. (d) M. Nonoyama, K. Nakajima, K. Nonoyama, Polyhedron 16 (1997) 4039. (e) M.A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero, M. Sansoni, J. Chem. Soc. Dalton Trans. (1995) 2865. (f) E.C. Constable, T.A. Leese, J. Organomet. Chem. 363 (1989) 419. (g) J. Vicenté, M.-T. Chicote, M.-D. Bermúdez, X. Soláns, M. Font-Altaba, J. Chem. Soc. Dalton Trans. (1984) 557. (h) J. Vicente, M.T. Chicote, Inorg. Chim. Acta 54 (1981) L259.

[4] J. Vicente, M.T. Chicote, M.D. Bermúdez, J. Organomet. Chem. 268 (1984) 191.

[5] P.A. Bonnardel, R.V. Parish, R.G. Pritchard, J. Chem. Soc. Dalton Trans. (1996) 3185.

[6] M.B. Dinger, W. Henderson, J. Organomet. Chem. 577 (1999) 219.

[7] M.B. Dinger, W. Henderson, J. Organomet. Chem. 577 (1998) 231.

[8] M.B. Dinger, W. Henderson, J. Organomet. Chem. 547 (1997) 243.

[9] (a) R.V. Parish, B.P. Howe, J.P. Wright, J. Mack, R.G. Pritchard, R.G. Buckley, A.M. Elsome, S.P. Fricker, Inorg. Chem. 35 (1996) 1659. (b) K. Ortner, U. Abram, Inorg. Chem. Commun. 1 (1998) 251.

[10] (a) W. Henderson, R.D.W. Kemmitt, S. Mason, M.R. Moore, J. Fawcett, D.R. Russell, J. Chem. Soc. Dalton Trans. (1992) 59. (b) W. Henderson, B.K. Nicholson, Polyhedron 15 (1996) 4015.

[11] M.B. Dinger, W. Henderson, B.K. Nicholson, W.T. Robinson, J. Organomet. Chem. 560 (1998) 169.

[12] W. Henderson, B.K. Nicholson, A.G. Oliver, J. Chem. Soc. Dalton Trans. (1994) 1831.

[13] W. Henderson, B.K. Nicholson, A.G. Oliver, Polyhedron 13 (1994) 3099.

[14] W. Henderson, A.G. Oliver, C.E.F. Rickard, L.J. Baker, Inorg. Chim. Acta 292 (1999) 260.

[15] W. Henderson, J. Fawcett, R.D.W. Kemmitt, C. Proctor, D.R. Russell, J. Chem. Soc. Dalton Trans. (1994) 3085.

[16] W. Henderson, A.G. Oliver, C.E.F. Rickard, Inorg. Chim. Acta 310 (2000) 242–247.

[17] T.-C. Cheung, T.-F. Lai, C.-M. Che, Polyhedron 13 (1994) 2073.

[18] S.L. Best, T.K. Chattopadhyay, M.I. Djuran, R.A. Palmer, P.J. Sadler, I. Sóvágó, K. Varnagy, J. Chem. Soc. Dalton Trans. (1997) 2587.

[19] G. Bandoli, D.A. Clemente, G. Marangoni, L. Cattalini, J. Chem. Soc. Dalton Trans. (1973) 886.

[20] (a) R. Bardi, A.M. Piazzesi, A. Del Pra, G. Cavinato, L. Toniolo, Inorg. Chim. Acta 75 (1983) 15. (b) S. Tollari, F. Demartin, S. Cenini, G. Palmisano, P. Raimondi, J. Organomet. Chem. 527 (1997) 93.

[21] (a) R. Navarro, E.P. Urriolabeitia, J. Chem. Soc. Dalton Trans. (1999) 4111. (b) R.G. Pearson, Inorg. Chem. 12 (1973) 712.

[22] M.B. Dinger, W. Henderson, J. Organomet. Chem. 560 (1998) 233.

[23] W. Henderson, A.G. Oliver, B.K. Nicholson, Inorg. Chim. Acta 298 (2000) 84.

[24] J.J. Peseck, W.R. Mason, Inorg. Chem. 22 (1983) 2958.

[25] R.V. Parish, J. Mack, L. Hargreaves, J.P. Wright, R.G. Buckley, A.M. Elsome, S.P. Fricker, B.R.C. Theobald, J. Chem. Soc. Dalton Trans. (1996) 69.

[26] R.H. Blessing, Acta Crystallogr. C51 (1995) 33.

[27] G.M. Sheldrick, SHELXS 96, SHELXS 97 and SHELXL 97, Programs for the solution and refinement of crystal structures, University of Göttingen, Germany, 1996–1997.